

CHEMICAL KINETICS
AND CATALYSIS

Peculiarities of Azobenzene Catalytic Hydrogenation in 2-Propanol Aqueous Solutions with Acid or Base Additives

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Abstract—It is shown experimentally that the hydrogenation of azobenzenes over a nickel skeleton catalyst in 2-propanol aqueous solutions proceeds selectively with the formation of aniline. It is pointed out that during the reaction, considerable participation of hydrogen bonded with active centers of a catalyst surface was observed. The competitive character of adsorption between the initial azo compound and aniline formed as a result of reaction is established. It is concluded that purposeful change of the azo group hydrogenation rate is possible by introducing acid or base additives into 2-propanol aqueous solution.

Keywords: azobenzene, aniline, hydrogen, nickel catalyst, hydrogenation, adsorption, hydrogenation rate control, isopropanol aqueous solutions, acetic acid, sodium hydroxide.

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INTRODUCTION

It is known [1, 2] that the nature and composition of solvent effect significantly the kinetic laws, rate, and selectivity of liquid-phase hydrogenation reactions. The solvent can change adsorptive ability and reactivity of hydrogen and a compound hydrogenated, the diffusion stages rate and solubility of reacting substances, solvent molecules can take part in the transition state in a catalytic reaction [3]. In liquid-phase hydrogenation reactions of substituted benzenes over nickel catalysts, even slight additives of acid or base effects significantly the rate of a process. The purposeful regulation of hydrogenation reaction rate and selectivity by the effect of solvent gives rise to the possibility of designing methods for the scientifically based selection of optimal catalytic systems for liquid-phase processes [3, 4]. The experimental base for the development of such optimization methods are the results of systematic investigations of substituted benzene hydrogenation reactions kinetics in solvents of different nature and composition.

The aim of this work was to study the reaction kinetic of azobenzene (AB) and 4-aminoazobenzene (4AAB) hydrogenation over nickel skeleton catalyst in 2-propanol aqueous solutions that included acetic acid and sodium hydroxide additives.

EXPERIMENTAL

Skeleton nickel obtained from nickel–aluminum alloy with a composition of Ni : Al : Fe = 47.5 : 50.2 : 0.3 wt % (Kandalaksha Metallurgical Works) was used

as a catalyst. The initial alloy was ground on a dispersor of impact-reflective action and was separated into fractions in a Gonnell air separator. To obtain active catalyst, the initial alloy was treated with 7.5 M aqueous solution of sodium hydroxide, as described in [5]. The obtained catalyst was washed with distilled water until a neutral reaction on phenolphthalein was obtained. For the experiments, the desired amounts of catalyst were hydrostatically weighed under water with an accuracy of ± 0.001 g. Before loading into the reactor, the catalyst was washed with solvent. The granulometric composition of the obtained powders was determined by conductimetric analysis using a Coultronics counter. Fractions of alloy with an average particle radius of 4.5–4.8 μm were used. The active skeleton nickel catalyst had a specific surface area of 90 ± 2 m^2/g and a porosity of 0.5 ± 0.06 cm^3/cm^3 Ni [5].

Our statistical investigations of the kinetic laws of the AB and 4AAB hydrogenation reactions over skeleton nickel were performed in a closed reactor with vigorous stirring of the liquid phase at the atmospheric pressure of hydrogen. The procedure for our kinetic experiments is described in [5]. The experimental conditions exclude the effect of external mass transfer on the reaction rate.

The azobenzene hydrogenation reactions were performed in 2-propanol aqueous solutions with different alcohol content. The amount of acetic acid and sodium hydroxide additives were varied from 0.005 up to 0.05 M, added to 2-propanol aqueous solution with an alcohol molar fraction of $x_2 = 0.68$. During each experiment, the volumes of hydrogen taken with time

were measured volumetrically, and the concentrations of initial compounds and reaction products, aniline and 1,4-phenylenediamine, were controlled by gas-liquid and liquid chromatography. The analysis of 4AAB and products of its reduction was performed on an LKhM-80.6 chromatograph with packed columns and a flame-ionization detector. Chromaton N-AW, 400–600 μm fraction covered with Lukopren G-1000 (7 wt %), was used as the solid phase; the length of a column was 1.5 m; the inert carrier gas was He; $t_{\text{col}} = 178^\circ\text{C}$; $t_{\text{vap}} = 320^\circ\text{C}$; $t_{\text{det}} = 240^\circ\text{C}$; and $p_{\text{He}} = 2.50$ atm. Our analysis of AB and its reduction products collected at different reaction times was performed on a Shimadzu liquid chromatograph under the following conditions: the carrier was an acetonitrile–water mixture with 30 vol % of acetonitrile; the rate of eluent in a column was $0.9\text{ cm}^3/\text{min}$; the temperature of a column thermostat was 30.8°C ; and the wavelength of the photometric detector was 322 nm. The time of aniline elution under these conditions was 330 ± 5 s, and the time of azobenzene elution was 1410 ± 30 s. The sensitivity of the analytic method was 10^{-8} mol in the reactor.

RESULTS AND DISCUSSION

It was shown experimentally that during AB and 4AAB hydrogenation over skeleton nickel catalyst in all of the solvents we used, the dependence of the rate on the degree of reaction completion corresponded to the kinetic curves of reactions that followed the direction of hydrogenation [6]. In alkali, neutral, and acidic solutions, the AB and 4AAB hydrogenation reaction proceeded without the accumulation of intermediate products in the reaction medium. In all solvents at high and medium concentrations of azobenzenes, areas with orders close to zero were observed on the kinetic curves. The rate of hydrogen consumption, $r_{\text{H}_2}^0$, at degrees of conversion of the initial compounds of less than 0.1 was chosen as the main kinetic characteristic of azobenzenes reactivity.

The observed values of rate constants of reaction, k_{obs}^0 , were also calculated in studying the 4AAB hydrogenation reaction, with allowance for the solubility and hydrogen partial pressures. The values of rate constants on an equally accessible surface, k_s^0 , were calculated according to the method described in [2, 3, 7]. Statistical analysis of the results showed that the errors in the values of rates, $r_{\text{H}_2}^0$, and rate constants, k_s^0 , were ~ 8 and $\sim 15\%$, respectively. The values of azobenzene adsorption were calculated according to the data from a chromatographic analysis of test portions collected during a reaction. In some cases, the activation energies were calculated according to the data on reaction constants or reaction rates at different temperatures.

In Figs. 1 and 2, the exemplary kinetic curves characterizing the change of amounts of hydrogen taken,

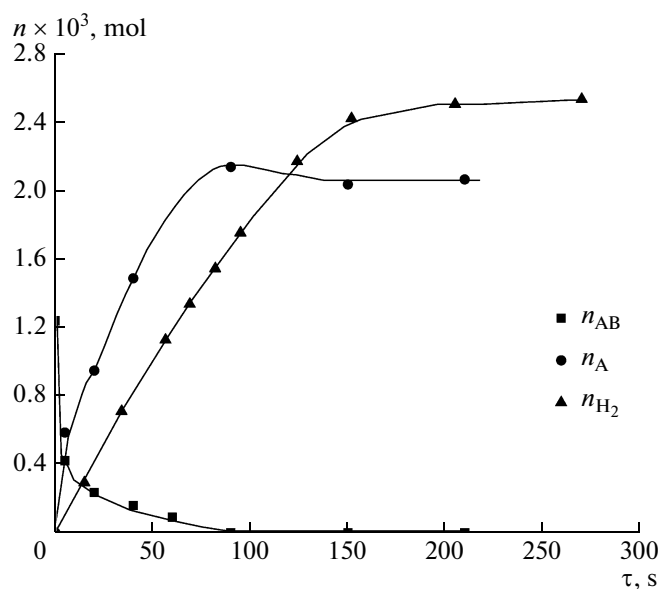


Fig. 1. Kinetic curves of the azobenzene hydrogenation reaction over skeleton catalyst in 2-propanol aqueous solution at the atmospheric pressure of hydrogen; $x_2 = 0.07$, $m_{\text{cat}} = 0.500 \pm 0.001$ g, $T_{\text{exp}} = 303$ K, $c_{\text{AB}}^0 = (1.4 \pm 0.1) \times 10^{-5}$ (mol/l).

AB, and aniline in solution during the reaction time are shown. As we can see from the presented data, the amount of aniline formed at the beginning of the reaction exceeds the amount of hydrogen taken from the gas phase. This indicates the participation in the reaction of hydrogen bonded by active centers of the catalyst surface. From the data shown in Figs. 1 and 2, it is obvious that the aniline concentration in the volume phase sharply increases at first, reaches a maximum, and then declines. It is typical that the lower the alcohol content in a solvent, the more quickly the maximum is achieved. For example, for 2-propanol aqueous solution with $x_2 = 0.07$, the maximum position corresponds to a time value of 75 ± 5 s, while upon transitioning to a solvent with $x_2 = 0.68$ it rises to 275 ± 15 s.

After complete AB conversion, hydrogen consumption continues and corresponds perfectly to the reaction stoichiometry upon completion of the reaction. The values for the initial reaction rates of hydrogenation and AB adsorption values in 2-propanol aqueous solutions are shown in Table 1.

It follows from these data that an increase in the water content in a solvent leads to an increase in both the AB hydrogenation rate and AB adsorption. It is known [8] that introducing acid or base additives into a 2-propanol aqueous solution also effects the rates of azobenzene hydrogenation.

The values for the initial rates of hydrogen consumption in AB and 4AAB hydrogenation reactions in 2-propanol aqueous solutions with the addition of

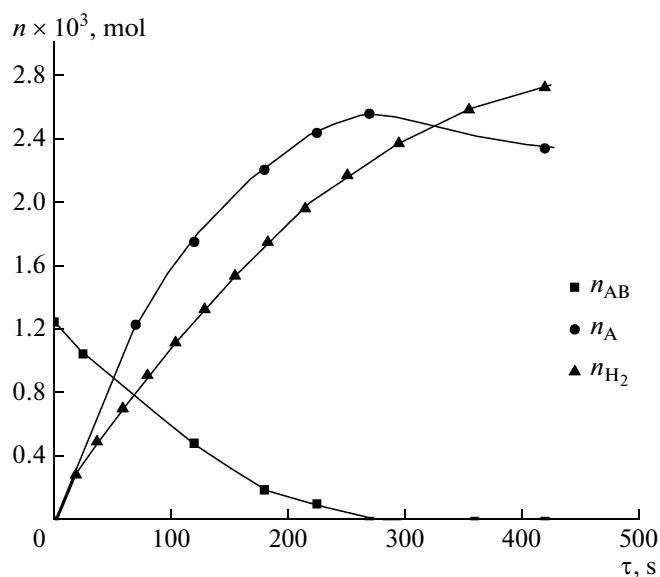


Fig. 2. Kinetic curves of azobenzene hydrogenation reaction over skeleton catalyst in 2-propanol aqueous solution at the atmospheric pressure of hydrogen; $x_2 = 0.68$, $m_{\text{cat}} = 0.500 \pm 0.001$ g, $T_{\text{exp}} = 303$ K, $c_{\text{AB}}^0 = (1.4 \pm 0.1) \times 10^{-5}$ (mol/l).

acetic acid and sodium hydroxide of different concentrations are shown in Table 2.

An analysis of the data shown in Table 2 reveals an increase in the reaction rate in the presence of acid, and a drop in the reaction rate in the presence of sodium hydroxide. The obtained relationships are in good agreement with the data of [9]. As was pointed out earlier, this can be explained by the change in the azobenzenes adsorption values upon the effect of solvent.

The 4AAB adsorption values in 2-propanol aqueous solutions with additions of acetic acid and sodium hydroxide, $x_2 = 0.68$, are shown in Table 3 along with the k_S^0 and E_S values.

As follows from the data of Table 3, the value of 4AAB adsorption in 2-propanol aqueous solution with the addition of 0.01 M sodium hydroxide increases by a factor of 1.8; in 2-propanol aqueous solution with the addition of 0.01 M acetic acid, the adsorption value increases by a factor of 1.6, relative to the alcohol aqueous solution.

Table 1. Initial hydrogenation rates and adsorption values of AB in 2-propanol aqueous solutions at 303 K, $m_{\text{cat}} = 0.500 \pm 0.001$ g

x_2	$r_{\text{AB}}^0 \times 10^5$, mol/s	a_R , mol/kg
0.68	0.80 ± 0.04	0.25 ± 0.05
0.07	16.4 ± 0.8	0.48 ± 0.07

On the other hand, according to the data of Table 2, the rate of 4AAB hydrogenation in 2-propanol aqueous solution with the addition of 0.01 M acetic acid is 1.7 times higher than the rate of 4AAB hydrogenation in a solvent with the addition of 0.01 M sodium hydroxide.

An analysis of the obtained data shows that the effect of acid and base additives to binary 2-propanol–water solvent on the kinetic laws of azobenzene hydrogenation reaction cannot be due solely to solvation interactions, or to the adsorption values of the hydrogenated compounds.

The rates of azo group hydrogenation both for AB and 4AAB when acid is present in the solvent are appreciably higher than for the presence of a base. For an alcohol–aqueous solution with the addition of 0.018 M of acetic acid, the AB hydrogenation rate is about 25 times higher than for 2-propanol aqueous solution with the addition of 0.012 M sodium hydroxide. An analogous situation is observed for 4AAB: the azo benzene group hydrogenation rate in the presence of an acid and a base at additive concentrations of 0.01 M differs by a factor of 1.7; in 0.02 M solutions it differs by a factor of 5.6.

Such changes in the azobenzene hydrogenation reaction rates in the presence of additives can be explained by the different ratios of individual forms of hydrogen sorbed as second reaction participate.

It is known [10] that the total reaction rate on a catalytic active surface containing a limited number of catalytic centers is composed of the reaction rates on each reaction center. According to the law of surface action [6], the hydrogenation reaction rate depends both on the adsorption values and on the reactivity of hydrogen active forms, relative to the initial compound. The change in the individual hydrogen forms' adsorption values under the influence of solvent can therefore substantially affect the observed rates of hydrogenation reactions. It has been shown that on nickel and a nickel catalyst surface, hydrogen sorbs in three individual forms: weakly bonded molecular, α , and two strongly bonded atomic forms, γ and β [11]. It is known [12] that the adsorption values of individual hydrogen forms change most drastically in the area of low additive concentrations. An analysis of the results of [13, 14] allows us to conclude that upon an increase in the pH of aqueous and alcohol solutions, the maximum adsorption values of the α form of hydrogen decline; for the β form, the dependence is of an extreme character with a maximum in the pH area of 9–10.

The values of maximum adsorption of the α and β forms of hydrogen at different pH values of aqueous solution at 303 K are shown in Table 4. Our results indicate that the character of the change in the rates and rate constants of azobenzene hydrogenation reactions in 2-propanol aqueous solutions with the addition of acetic acid and sodium hydroxide qualitatively agree with the change in the maximum values of adsorption of the

Table 2. Values of the AB and 4AAB hydrogenation reaction rates in 2-propanol aqueous solutions ($x_2 = 0.68$)

Additive	C, mol/l	$r_{\text{H}_2}^0 \times 10^5$, mol/(g s)
AB		
—	0	1.8 ± 0.1
CH ₃ COOH	0.001	1.3 ± 0.1
	0.018	3.6 ± 0.2
	0.036	4.5 ± 0.1
NaOH	0.004	0.54 ± 0.04
	0.012	0.14 ± 0.01
4AAB		
—	0	2.1 ± 0.1
CH ₃ COOH	0.01	6.1 ± 0.4
	0.02	7.8 ± 0.4
NaOH	0.01	3.5 ± 0.2
	0.02	1.38 ± 0.09

Note: C is an additive concentration.

Table 3. Kinetic parameters of the 4AAB hydrogenation reaction on skeleton nickel in 2-propanol aqueous solution at 303 K ($x_2 = 0.68$)

Additive	a_{R} , mol/kg	k_{S}^0 , s ⁻¹	E_{S} , kJ/mol
0.01 M CH ₃ COOH	0.8 ± 0.1	130 ± 15	17 ± 5
—	0.5 ± 0.1	41 ± 8	42 ± 6
0.02 M NaOH	0.9 ± 0.1	29 ± 6	(32 ± 5)

Note: Experimental conditions were $p_{\text{H}_2} = 0.1$ MPa; $m_{\text{cat}} = 0.625 \pm 0.001$ g; $r_{\text{cat}} = 4.7$ μm ; $V_{\text{liq. ph.}} = 102$ cm³; $m_{4\text{AAB}} = 0.250 \pm 0.005$ g. The value in parentheses is the activation energy for 2-propanol aqueous solution, $x_2 = 0.68$, 0.01 M NaOH.

Table 4. Maximum values of adsorption, a_{m} , of α and β forms of hydrogen, adsorbed on skeleton nickel in water in dependence on pH and the rate constant of the 4AAB hydrogenation reaction in 2-propanol aqueous solutions at 303 K

pH	a_{m} , cm ³ H ₂ /g Ni	
	α form	β form
6.0	2.38	8.04
7.0	1.9	9.05
9.0	1.63	10.53
10.0	1.49	10.41
11.0	1.49	10.15
12.0	1.6	9.67

Note: pH change from 6.0 to 12.0 leads to k_{S}^0 change from 130 to 29 s⁻¹.

weakly-bonded α form molecule, and the strongly bonded β form of sorbed atomic hydrogen.

According to the data in Table 4, an increase in the fraction of weakly bonded hydrogen should lead to an increase in the rate constants of the azobenzene group hydrogenation reaction, while an increase in the content of atomic forms should lead to a decrease. This has been confirmed experimentally: the 4AAB hydrogenation reaction rate constants rise sharply upon transitioning from neutral water–alcohol solvent to an acidic medium and fall in the presence of sodium hydroxide.

CONCLUSIONS

Our studies allow us to conclude that the purposeful regulation of azo group hydrogenation rate on the surface of skeleton nickel catalyst is possible by adding acid or base to a solvent.

It should be noted that at the presence of very low amounts of additives (e.g., in the presence of 0.001 M of acetic acid), the AB azo group hydrogenation reaction rate declines, while for 4AAB in the presence of 0.01 M of sodium hydroxide, the rate rises relative to 2-propanol aqueous solution without additives. This experimental finding still has no definite explanation.

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